09/937686

00270

Attorney's Docket No.: JYG151USA

JC09 Rec'd PCT/PTO 28 SEP 2001

TRANSMITTAL LETTER TO THE U.S. ELECTED OFFICE
(EO/US) - ENTRY INTO NATIONAL STAGE UNDER 35 USC 371

PCT/GB00/01251	31 March 2000	31 March 1999
International Application No	International Filing Date	Priority Date Claimed

EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONS
Title of Invention

Peter Anthony Tasker	David James White
25 Braid Avenue	3 Roachill Close
Edinburgh	Altrincham, Cheshire
United Kingdom	United Kingdom
Citizenship: United Kingdom	Citizenship: United Kingdom

Applicant(s), Residence Addresses and Citizenship for EO/US

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231
Attn. EO/US

Sir:

Applicant herewith submits to the United States Elected Office (EO/US) the following items under 35 USC 371:

(1) This express request to immediately begin national examination procedures (35 USC 371(f)).

(2) A copy of the international application: one cover page, 22 pages of specification, three pages of claims, and two pages of International Search Report.

(3) A copy of the three page Request form.

(4) A First Preliminary Amendment which cancels the multiple dependent claim and which should be entered **before** the calculation of the filing fee.

(5) A Second Preliminary Amendment.

(6) Our check in the amount of $430 covering the basic national fee as set forth in 37 CFR 1.492(a)(5) for a **small entity (nonprofit organization - university)**. (18 claims in total; 1 independent; and no multiple dependent).

EK992698259US

Copies of the following miscellaneous items are also enclosed:

(7) Copy of the three page Demand for International Preliminary Examination.

(8) Copy of the five page Written Opinion dated December 21, 2000.

(9) Copy of the Applicants' eight page Response to the Written Opinion dated May 21, 2001.

(10) Copy of the eleven page International Preliminary Examination Report, dated June 15, 2001.

The Combined Declaration and Power of Attorney form will be filed by the appropriate deadline under 37 CFR §1.495(c)(2) with the surcharge under 37 CFR §1.492(e).

Please charge any additional fees which may be required to effect entry into the National Phase and credit any overpayment to our deposit account 08-3040.

Please direct all communications concerning this application to the undersigned.

Respectfully submitted,
Howson and Howson
Attorneys for the Applicant

By _____

William Bak
Registration No. 37,277
Spring House Corporate Center
Box 457
Spring House, PA 19477
(215) 540-9216

preliminary amendment, the application has six claims in total, one independent claim, and no multiple dependent claims.

Charge any additional fees due to our deposit account no. 08-3040.

Respectfully submitted,
Howson and Howson
Attorneys for Applicant

By _____
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Box 457
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PTO/SB/11 (12-97)
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STATEMENT CLAIMING SMALL ENTITY STATUS (37 CFR 1.9(f) & 1.27(d))--NONPROFIT ORGANIZATION	Docket Number (Optional)

Applicant, Patentee, or Identifier: Peter A. Tasker and David J. White
Application or Patent No.: PCT/GB00/01251
Filed or Issued:
Title: EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONS

I hereby state that I am an official empowered to act on behalf of the nonprofit organization identified below:
NAME OF NONPROFIT ORGANIZATION The University Court of the University of Edinburgh
ADDRESS OF NONPROFIT ORGANIZATION Old College, South Bridge, Edinburgh, EH8 9YL, United Kingdom

TYPE OF NONPROFIT ORGANIZATION:
☒ UNIVERSITY OR OTHER INSTITUTION OF HIGHER EDUCATION

☐ TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 U.S.C. 501(a) and 501(c)(3))

☐ NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED STATES OF AMERICA
(NAME OF STATE _____)
(CITATION OF STATUTE _____)

☐ WOULD QUALIFY AS TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 U.S.C. 501(a) and 501(c)(3)) IF LOCATED IN THE UNITED STATES OF AMERICA

☐ WOULD QUALIFY AS NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED STATES OF AMERICA IF LOCATED IN THE UNITED STATES OF AMERICA
(NAME OF STATE _____)
(CITATION OF STATUTE _____)

I hereby state that the nonprofit organization identified above qualifies as a nonprofit organization as defined in 37 CFR 1.9(e) for purposes of paying reduced fees to the United States Patent and Trademark Office regarding the invention described in:

☐ the specification filed herewith with title as listed above.
☒ the application identified above.
☐ the patent identified above.

I hereby state that rights under contract or law have been conveyed to and remain with the nonprofit organization regarding the above identified invention. If the rights held by the nonprofit organization are not exclusive, each individual, concern, or organization having rights in the invention must file separate statements as to their status as small entities and that no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37CFR 1.9(c) if that person made the invention, or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern, or organization having any rights in the invention is listed below:

complete >
☒ no such person, concern, or organization exists.
☐ each such person, concern, or organization is listed below.

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

NAME OF PERSON SIGNING MELVYN DAVID CORNISH
TITLE IN ORGANIZATION OF PERSON SIGNING Deputy Secretary to the University
ADDRESS OF PERSON SIGNING Old College, South Bridge, Edinburgh EH8 9YL
SIGNATURE _____ DATE 10 February 2001

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.

00270

JYG151USA

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:	)	
	)	Examiner:
Tasker et al.	)	
	)	Group Art Unit:
Application No.:	)	
	)	
Corresponding International Filing No.:	)	
PCT/GB00/01251	)	
	)	
Filed: Herewith	)	
	)	
For: EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONS	)	
	)	September 28, 2001

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

FIRST PRELIMINARY AMENDMENT

Sir:

Before calculating the filing fee, please amend the above-identified patent application as follows.

In the Claims

Cancel multiple dependent claims 4, 6, 8 and 10.

REMARKS

Please enter this preliminary amendment before calculating the filing fee. This preliminary amendment cancels all the multiple dependent claims. Thus, after entry of this

JYG151USA

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:	)	
	)	Examiner:
Tasker et al.	)	
	)	Group Art Unit:
Application No.:	)	
	)	
Corresponding International Filing No.: PCT/GB00/01251	)	
	)	
Filed: Herewith	)	
	)	
For: EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONS	)	September 28, 2001

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

SECOND PRELIMINARY AMENDMENT

Sir:

Please amend the above-identified patent application as follows.

The format of this Amendment complies with 37 CFR §1.121 "Manner of making amendments in applications" as amended on November 7, 2000 pursuant to the "Patent Business Goals Final Rule". Thus, according to 37 CFR §1.121(b)(ii) & (c)(i), amended paragraphs of the specification and amended claims are provided in a form "without markings"; and according to 37 CFR §1.121(b)(iii) & (c)(ii), the amended paragraphs of the specification and amended claims are also provided, on a separate page, "marked up" to show the changes.

In the Specification:

On page 1, amend the third paragraph as follows [format corresponding to 37 CFR §1.121(b)(ii), ie. "**without markings**"] :

Current solvent extraction technology is based on a system in which an acidic extractant is used to remove a metal cation from an aqueous feed stream. The metal n^+ cation is replaced by n protons and the anion is left in the solution. The overall effect on the feed stream is to replace a metal salt MX with a mineral acid H_nX and this leads to an increase in the acidity of the aqueous feed stream.

On page 7, line 24, to page 8, line 5, amend the paragraphs as follows [format corresponding to 37 CFR §1.121(b)(ii), ie. "**without markings**"] :

In each case the overall reaction is the same. The overall mass balance for this system is:

$$MS + 1½O_2 + H_2O + 2NH_3 + \text{Power} = M + (NH_4)_2SO_4$$

In a waste remediation application, for example of metal salts from acid mine drainage streams, the overall mass balance is:

$$MSO_4 + H_2O + 2NH_3 + \text{Power} = M + (NH_4)_2SO_4 + ½O_2$$

In the Abstract

Please enter the abstract on a separate page as attached.

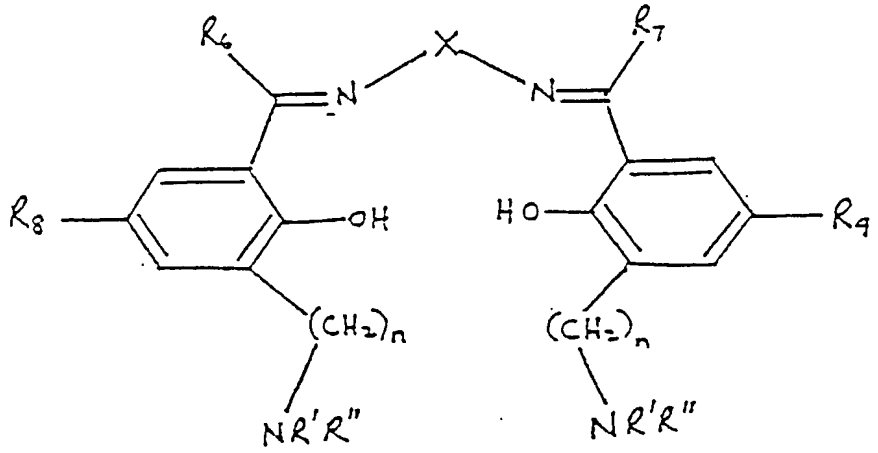
In the Claims

Amend claims 1, 5, 7 and 9, as follows. [Format corresponding to 37 CFR §1.121(c)(i), ie. "**without markings**".]

1(Amended). A method of extracting both the cation(s) and anion(s) of a metal salt from an aqueous medium, the method comprising the step of contacting the aqueous medium with a bifunctional ligand capable of binding both said cation(s) and said anion(s) so as to form a complex comprising said ligand and said cation(s) and anion(s).

5(Amended). A method according to claim 14, comprising the further steps of: contacting the ligand-bound salt with an aqueous ammoniacal solution to produce an aqueous ammoniacal solution of the metal salt; and electrolysing said solution to produce elemental metal and an ammonium salt.

7(Amended). A method according to claim 15, wherein the ligand has the following formula:



where:

X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n=2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

R'R" are tertiary amine groups optionally forming a heterocyclic ring.

9(Amended). A method according to claim 17, comprising the further step of contacting the ligand-bound anion(s) with an ammoniacal solution, to neutralise said solution and produce an ammonium salt.

Add new claims 11-22, as follows.

11(New). A method according to claim 1, further comprising the steps of selectively stripping and recovering said cation(s) and said anion(s) from said complex; and recovering said ligand, free of said cation(s) and anion(s), for future use.

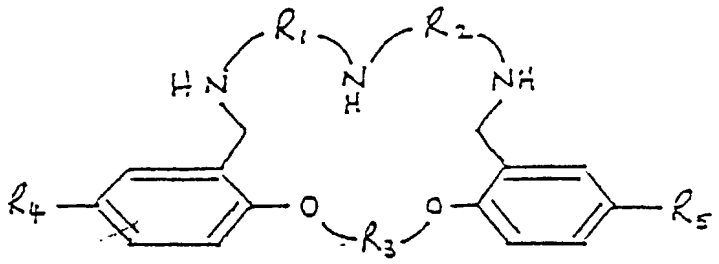
12(New). A method according to claim 11, further comprising the steps of:

adding a water-immiscible extraction medium to said aqueous medium, wherein the ligand has a greater affinity for said water-immiscible extraction medium than it does for said aqueous medium and whereby said ligand with said cation(s) and said anion(s) bound thereto is partitioned preferentially in a water-immiscible phase; and

separating said water immiscible phase with said ligand-bound cation(s) and anion(s) therein from said aqueous medium.

13(New). A method according to claim 11, wherein the ligand is immobilized on or within a solid support.

14(New). A method according to claim 1, wherein the ligand is of the following formula:



where R_1, R_2, R_3 are, independently, substituted C_2 to C_4 linkages; and

R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

15(New). A method according to claim 1, wherein the ligand has a cation binding site comprising at least one coordinating acid group and an anion binding site comprising at least one protonatable base.

16(New). A method according to claim 12, wherein the ligand has a cation binding site comprising at least one coordinating acid group and an anion binding site comprising at least one protonatable base.

17(New). A method according to claim 15, comprising the further steps of: contacting the ligand-bound salt with a strong acid to protonate the ligand and release the metal cation(s); and electolysing the resulting solution to produce elemental metal.

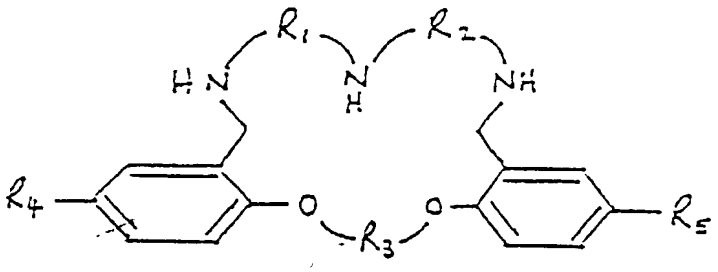
18(New). A method according to claim 7, comprising the further steps of: contacting the ligand-bound salt with a strong acid to protonate the ligand and release the metal cation(s); and electolysing the resulting solution to produce elemental metal.

19(New). A method according to claim 18, comprising the further step of contacting the ligand-bound anion(s) with an ammoniacal solution, to neutralise said solution and produce an ammonium salt.

20(New). A method according to claim 7, wherein NR'R" is selected from the group consisting of a morpholine ring and a piperdine ring.

21(New). A method according to claim 19, wherein NR'R" is selected from the group consisting of a morpholine ring and a piperdine ring.

22(New). A method according to claim 12, wherein the ligand is of the following formula:



where R_1, R_2, R_3 are, independently, substituted C_2 to C_4 linkages; and

R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

Version of Amended Paragraphs of Specification with Markings to Show Changes Made Corresponding to 37 CFR §1.121(b)(iii)

On page 1, amend the third paragraph as follows [format corresponding to 37 CFR §1.121(b)(iii), ie. "with markings"] :

Current solvent extraction technology is based on [the reaction scheme shown schematically in Figure 1. In this] a system in which an acidic extractant is used to remove a metal cation from an aqueous feed stream. The metal n^+ cation is replaced by n protons and the anion is left in the solution. The overall effect on the feed stream is to replace a metal salt MX with a mineral acid H_nX and this leads to an increase in the acidity of the aqueous feed stream.

On page 7, line 24, to page 8, line 5, amend the paragraphs as follows [format corresponding to 37 CFR §1.121(b)(iii), ie. "with markings"] :

In each case the overall reaction is the same [, and may be represented by the reaction scheme illustrated in Figure 2]. The overall mass balance for this system is:

$$MS + 1½O_2 + H_2O + 2NH_3 + \text{Power} = M + (NH_4)_2SO_4$$

In a waste remediation application, for example of metal salts from acid mine drainage streams, [the reaction scheme is illustrated in Figure 3;] the overall mass balance is:

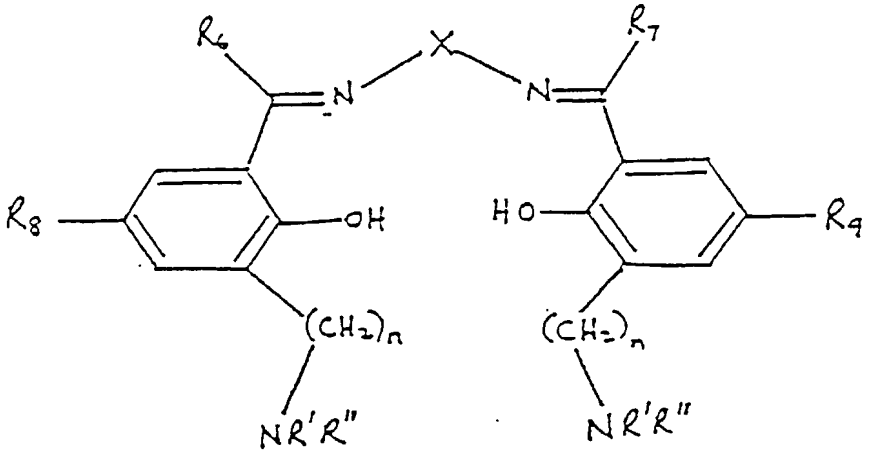
$$MSO_4 + H_2O + 2NH_3 + \text{Power} = M + (NH_4)_2SO_4 + ½O_2$$

Version of Amended Claims
with Markings to Show Changes Made
Corresponding to 37 CFR §1.121(c)(ii)

1(Amended). A method of extracting both the cation(s) and anion(s) of a metal salt from an aqueous medium, the method comprising the [steps] step of [:] contacting the aqueous medium with a bifunctional ligand capable of binding both said cation(s) and said anion(s) so as to form a complex comprising said ligand and said cation(s) and anion(s) [; selectively stripping and recovering said cation(s) and said anion(s) from said complex; and recovering said ligand, free of said cation(s) and anion(s), for future use].

5(Amended). A method according to claim [4] 14, comprising the further steps of: contacting the ligand-bound salt with an aqueous ammoniacal solution to produce an aqueous ammoniacal solution of the metal salt; and electrolysing said solution to produce elemental metal and an ammonium salt.

7(Amended). A method according to claim [6] 15, wherein the ligand has the following formula:



where:

X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n=2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

R'R" are tertiary amine groups optionally forming a heterocyclic ring.

9(Amended). A method according to claim [8] 17, comprising the further step of contacting the ligand-bound anion(s) with an ammoniacal solution, to neutralise said solution and produce an ammonium salt.

REMARKS

After entry of the first and secondary preliminary amendments, the pending claims are claims 1-3, 5, 7, 9 and 11-22. This includes eighteen claims in total, one independent claim, and no multiple dependent claims.

The claim set published in the International application is being utilized as the as-filed claims from which the claim amendments are made. The amendments of the specification and claims correspond to amendments presented in a response to a written opinion in the International application. To this end, the specification has been amended to delete reference to Figures 1-3, and all the pending claims are supported by the disclosure of claims 1-10 as published in the International application. The attached abstract is substantially identical to the abstract published on the cover page of the published International application. Thus, no new subject matter is added by any of the amendments.

Applicants respectfully request consideration of claims 1-3, 5, 7, 9 and 11-22.

Charge any additional fees due to our deposit account no. 08-3040.

Respectfully submitted,
Howson and Howson
Attorneys for Applicant

By _____
William Bak
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Spring House Corporate Center
Box 457
Spring House, PA 19477
(215) 540-9216

#6 Brief

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of)
)
Tasker et al.)
)
Application No.: 09/937,686)
)
Filed: September 28, 2001)
)
For: EXTRACTION OF METAL)
SALTS FROM AQUEOUS)
SOLUTIONS)

Examiner:

Group Art Unit:

CERTIFICATE UNDER 37 CFR 1.8(a)
I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail on the date indicated below in an envelope addressed to:. Commissioner for Patents
Washington, DC 20231.

Signature _____
Date 3-27-2002

Commissioner for Patents
Washington, DC 20231

THIRD PRELIMINARY AMENDMENT

Sir:

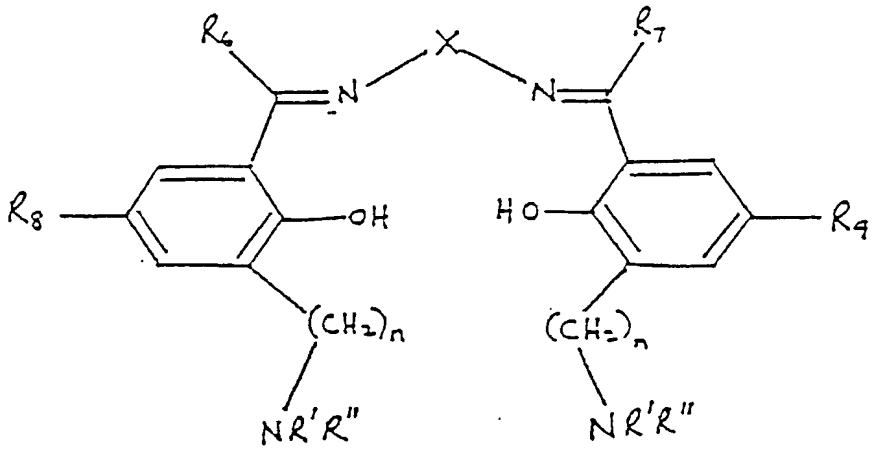
Please amend the above-identified patent application as follows.

The format of this Amendment complies with 37 CFR §1.121 "Manner of making amendments in applications" as amended on November 7, 2000 pursuant to the "Patent Business Goals Final Rule". Thus, according to 37 CFR §1.121(b)(ii) & (c)(i), amended paragraphs of the specification and amended claims are provided in a form "without markings"; and according to 37 CFR §1.121(b)(iii) & (c)(ii), the amended paragraphs of the specification and amended claims are also provided, on a separate page, "marked up" to show the changes.

In the Claims:

Add new claims 23 and 24, as follows.

23(New). A method according to claim 1, wherein the ligand has the following formula:



where:

X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

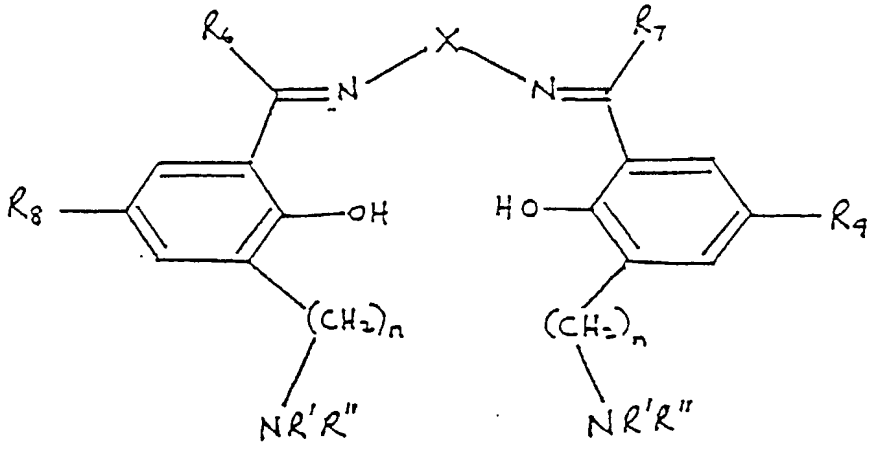
n=1, 2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

NR'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring;

provided that, when NR'R" is a morpholine group and R_6 and R_7 are H, R_8 and R_9 are not $-CH_3$.

24(New). A ligand having the following formula:



where:

X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n=1, 2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

NR'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring;

provided that, when NR'R" is a morpholine group and R_6 and R_7 are H, R_8 and R_9 are not $-CH_3$.

REMARKS

Claims 23 and 24 have been added. Thus, the pending claims are now claims 1-3, 5, 7, 9 and 11-24. This includes twenty claims in total, two independent claims, and no multiple dependent claims.

The formula for the ligand claimed in claims 23 and 24 is disclosed on page 6 of the present application. No new matter was added.

Applicant respectfully requests consideration of claims 1-3, 5, 7, 9 and 11-24.

Charge any additional fees due to our deposit account no. 08-3040.

Respectfully submitted,
Howson and Howson
Attorneys for Applicant

By _____
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Box 457
Spring House, PA 19477
(215) 540-9216

Rec'd PCT/PTO 28 SEP 2001 09/937686

EXTRACTION OF METAL SALTS

Field of the invention

This invention relates to the extraction of metal salts from aqueous solutions. More specifically it relates to methods for extracting metal cations and their associated anions which avoid returning any ionic species to the solution, thus leaving the acidity of the solution unchanged and purifying it by deionisation. Methods according to the invention are of use particularly (though not exclusively) in waste remediation and in the recovery of metals from primary sources.

Background

Two main methods are currently used for the extraction of metallic ions from solution. Both involve the use of an extractant reagent: in the first method this is mixed with the solution from which the metal ions are to be removed ("solvent extraction"), and in the second it is immobilised on a solid support.

Current solvent extraction technology is based on a system in which an acidic extractant is used to remove a metal cation from an aqueous feed stream. The metal n^+ cation is replaced by n protons and the anion is left in the solution. The overall effect on the feed stream is to replace a metal salt MX with a mineral acid H_nX and this leads to an increase in the acidity of the aqueous feed stream.

This type of reaction is widely used for the extraction of copper from oxidic ores, the acid introduced into the stream reacting with insoluble metal oxides to give soluble metal salts. Indeed, this reaction scheme is particularly suited to the extraction of metals from metal oxides since the overall reaction has a perfect mass balance equation:

$$MO + Power = M + \tfrac{1}{2}O_2$$

However, this extraction technique suffers from a number of shortcomings. For instance, it is not suitable for use in relation to feed streams which have a very high metal tenor (i.e. a high concentration of metal in the feed), since removal of metal ions rapidly decreases the pH of the solution, and this renders the extractant ineffective. A similar effect is observed if the feed stream itself has a low pH value. For the same reason, if acid is not consumed in the leach process, pH will decrease and the extractant will become ineffective unless action is taken to neutralise the stream. This is particularly important in oxidative pressure leaching of sulfidic metal ores and biological leaching of sulfidic ores, where oxygen or oxygen and microbes are used to convert sulfides into sulfates without consumption of acid. Furthermore, the waste water from such extraction techniques cannot be discharged to the environment after metal extraction since, again, neutralisation of the acid would be required prior to discharge.

As far as solid supported reagents are concerned, most of these operate as ion exchange materials. The reagent on the solid phase support binds a metal cation and releases a cation (usually Na^+ or a proton) to the aqueous phase. Thus, the metal ion in solution is replaced either by sodium ions which increases the salinity of the solution, or by protons which reduce the pH of the feed solution. In either case the anion is left in solution.

We have now found that it is possible, through careful engineering of the ligand, to extract metal cations from a solution and simultaneously to extract their associated anions. This method has the advantage that the whole metal salt is removed from the feed stream, the pH of the stream is unaltered, and no additional species are added to the feed stream. Additionally, the ligands we have developed permit both the anions and the cations to be recovered by stripping methods, with the result that the ligand may then be reused.

The ligands of use in the method of the invention have binding sites for both cations and anions, in contrast to the vast majority of existing ligands which

bind only cations. A small number of bifunctional ligands have been identified in the past, and some of these are reviewed in "Comprehensive Supramolecular Chemistry" (1996) Chapter 18 "Simultaneous Binding of Cations and Anions" (Manfred T. Reetz) pp 553-562. A common feature of the ligands described is that the cation binding sites are all ordinary or azo crown ethers. A variety of groups are suggested for anion binding, such as polyammonium, guanidine, boronic acid and cobalticinium. Crown ethers are also suggested as the cation binding site of bifunctional ligands by Ezzidin et al (J. Chem. Soc [1992] 61-64), Olsher et al (J. Am. Chem. Soc. 113 [1991] 6570-6574) and Flack et al (J. Chem. Soc., Chem. Commun. [1993] 399-401). Nitrogen-containing groups provide the anion binding sites of the ligands proposed by Ezzidin et al and Flack et al, while Olsher et al use alcohol groups.

Alternative ligands are proposed by Hogerhide et al (Inorg. Chem. 35 [1996] 1185-1194), Pelizzi et al (J. Chem. Soc., Perkin Trans. 2 [1998] 1307-1311) and Savage et al (J. Am. Chem. Soc. 116 [1994] 4069-4070), but as with the papers relating to crown ether ligands referred to above, there is no suggestion of recovery of both anions and cations in any ready manner. The target metal salts are almost exclusively those containing small monovalent metal cations such as Na^+ and K^+. Transition metal salts are not considered.

Shanmuga et al (Acta Crystallographica Section C [1999] 94-97) mention a ligand identical with that identified in the description below as ligand 4. However, the authors propose this for use solely in forming binuclear metal complexes as models of metal binding in biology. There is no suggestion or intention to bind either anions or metal salts. Additionally, no real evidence of metal binding is provided.

Summary of the invention

The invention seeks to overcome the drawbacks associated with the existing methods for metal salt removal, and provides a method of extracting

both the cation(s) and anion(s) of a metal salt from an aqueous medium, the method comprising the steps of: contacting the aqueous medium with a bifunctional ligand capable of binding both said cation(s) and said anion(s) so as to form a complex comprising said ligand and said cation(s) and anion(s); selectively stripping and recovering said cation(s) and said anion(s) from said complex; and recovering said ligand, free of said cation(s) and anion(s), for future use. The method is particularly suitable for use with transition metal salts (including salts of the lanthanides and actinides)

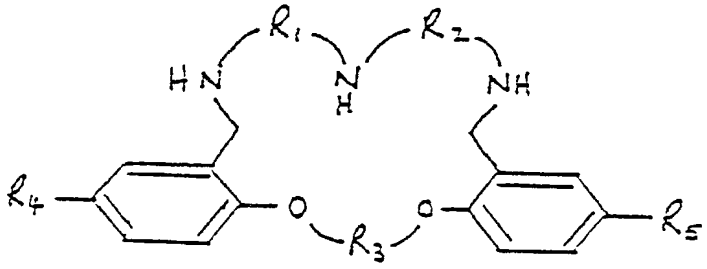
The method of the invention may either be carried out as a solvent extraction process of by use of a solid phase ligand. In the solvent extraction process, the ligand preferably has a greater affinity for a water-immiscible extraction medium than it does for said aqueous medium, which may readily be achieved by judicious choice of side chains to render the ligand substantially hydrophobic. Preferably, the method involves the steps of adding the water-immiscible extraction medium to the aqueous medium (whereby the ligand with the cation(s) and anion(s) bound thereto is partitioned preferentially a water-immiscible phase), and separating the water-immiscible phase with the cation(s) and anion(s) therein from the aqueous phase.

For operation as a solid-phase extractant, the ligand may simply be immobilised on a solid support. By contacting the support-bound ligand with the aqueous feed stream, the metal salt may thereby be removed in a simple one-step process, without the need for a separation step. A solid-phase extraction is particularly useful for sequestering species from dilute solutions, in respect of which solvent extraction tends to be cumbersome and inefficient. The method will be particularly useful in the remediation of contaminated streams, especially those which are acidic, for example in the removal of actinide salts produced in the nuclear industry.

In both solvent and solid based methods, metal cations and their associated anions removed from the solution simultaneously, and no species are returned to the feed stream in their place. This makes the processes suitable for

use in many applications for which the prior art methods are unsuitable, since the pH of the feed stream is unaltered, the feed stream is purified by de-ionisation, and, within limits that will be defined by the specific reagent used in the process, metal cations and anions can be extracted at low pH without further lowering the pH. For the sake of simplicity and clarity the invention will hereafter be described principally with respect to solvent extraction processes, but the skilled man will have no difficulty in adapting the techniques for use in analogues solid-phase systems.

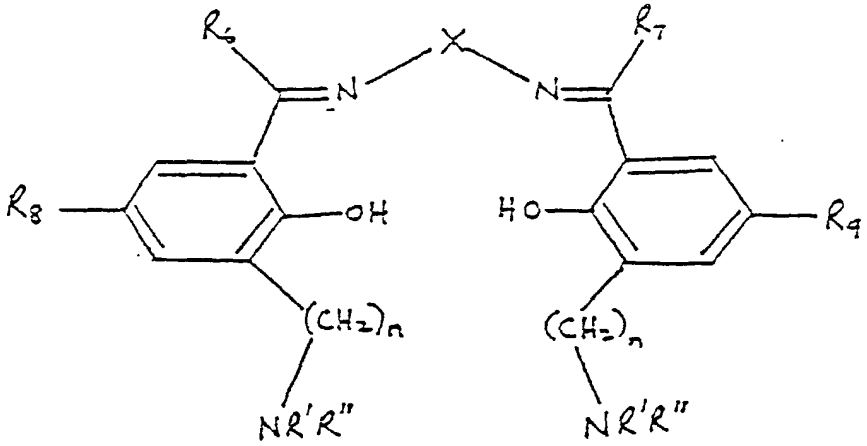
The applicants have developed two distinct classes of ligand for use in the processes of the invention. The first class ("Type I") have the following general formula:



where: R_1, R_2 and R_3 are, independently, optionally substituted C_2 to C_4 linkages;

R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

The second class ("Type II") have the formula:



where:

X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n = 2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

NR'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring.

In both cases the side chains (R_4, R_5, R_6, R_7, R_8 and R_9) do not take part in ligand binding, and may be freely chosen with reference to the nature of the extraction medium in order to afford maximum solubility of the ligand therein. Hydrocarbon extraction media are preferred, and thus the side chains will normally confer hydrophobicity.

In the Type II ligands, it is believed that the metal cation binds first to the nitrogen atoms of the C=N groups and to the phenolic oxygen atoms. The

phenolic protons are then displaced and protonate the nitrogen atoms of the tertiary amine groups, producing a positively charged binding site for the anion. The precise binding mechanism for the Type I ligands has yet to be elucidated.

Use of either class of ligand is effective to remove both the cations and anions of a metal salt from the feed stream. When decontamination of the feed stream is the sole aim, removal of the metal salt may be regarded as an end in itself. In most cases, however, it is desired to extract the cations as elemental metal, and indeed this is the primary aim of ore extraction methods. A major advantage of the method of the invention is that the anion may also retrieved; for instance the anion (such as sulphate) may be precipitated as an ammonium salt, which may then be used as fertiliser. As a result, this ligand is regenerated in unbound form, and may be recycled for future use.

The method of cation and anion precipitation depends on the class of ligand. For Type I ligands, contact with an aqueous ammoniacal solution liberates an ammoniacal solution of the metal salt from which the metal can be electrolysed. The electrolysis step produces metal and acid. Continual addition of ammonia to the system is required to neutralise the acid produced, and a by product of the reaction is an ammonium salt. For Type II ligands, the metal cation may also be recovered by contacting with strong acid. The metal cation M^{n+} in the hydrocarbon solution is replaced by n protons generating the 'acid' form of the reagent LH_nX. This allows electrolysis of the metal from an acidic medium. The resulting solution is then contacted with ammonia solution, regenerating the reagent L and producing an ammonium salt as a by product.

In each case the overall reaction is the same. The overall mass balance for this system is:

$$MS + 1\frac{1}{2}O_2 + H_2O + 2NH_3 + Power = M + (NH_4)_2SO_4$$

In a waste remediation application, for example removal of metal salts

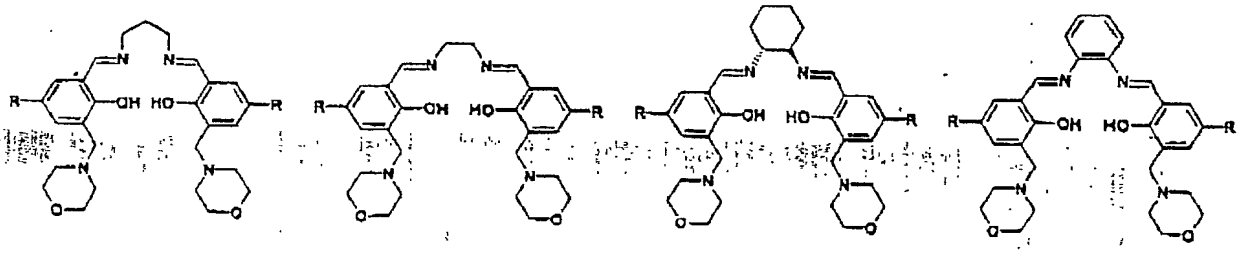
from acid drainage streams, the overall mass balance is:

$$MSO_4 + H_2O + 2NH_3 + Power = M + (NH_4)_2SO_4 + \tfrac{1}{2}O_2$$

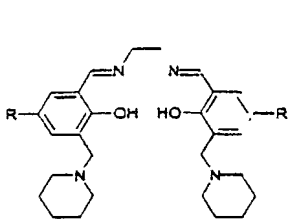
The Type 1 ligands are known in the literature, though not for the purpose of removing metal salts from aqueous solutions as in the present invention; their synethesis will therefore not be described herein. To illustrate the efficacy of ligands of this type in removing metal salts from aqueous solution, a 0.1M solution in toluene of Type I ligand ($R_1 = R_2 = R_3 = -CH_2CH_2-$; $R_4=R_5=C_9H_{19}$) was contacted with an 0.1M aqueous solution of nickel sulfate. A light blue toluene solution was formed, analysis of which showed that approximately 80% of both Ni^{2+} and SO_4^{2-} ions had been transferred to the organic phase.

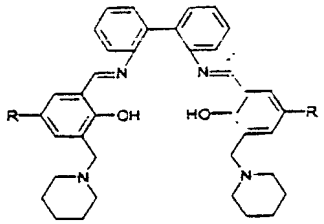
Detailed description

The invention is described hereinafter in more detail with reference to the synthesis and activity of various ligands of the Type II formula. The following is a representative sample of various different Type II ligands:



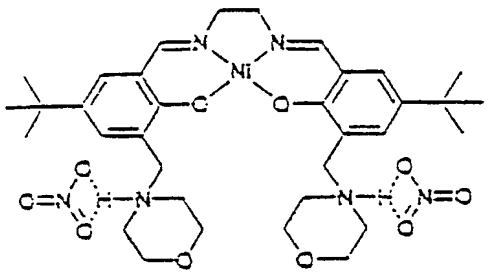
Me	4	5	6	7
TBu	8	9	10	11
Nonyl	12	13	14	15

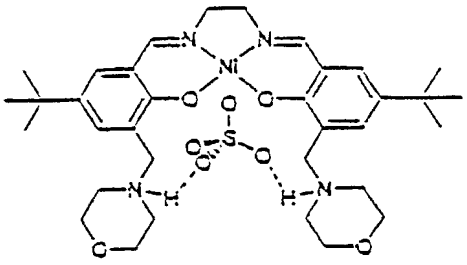




Me	16	17
Tbu	18	19
Nonyl	20	21

By way of example, X-ray structure studies have demonstrated that the mode of binding of nickel nitrate and nickel sulfate to ligand number 8 is generally as shown below. As will be seen, the protons liberated from the phenolic groups in the metal binding site remain incorporated in the ligand, and protonate the basic pendant morpholine groups to form the anion binding site(s).



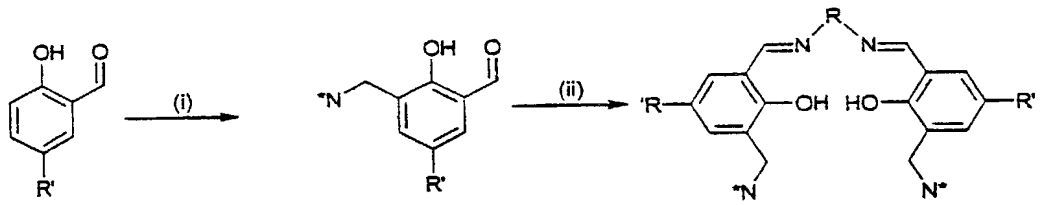


Solvent extraction studies have been carried out to characterise the extraction behaviour of these ligands, and are summarised in the experimental sec tion below. In order for the extraction system to be viable a plateau pH range must exist at which both metal cation and sulphur are extracted with 100% efficiency. This can be engineered into the molecule by judicious choice of chelating moiety and internal base.

Synthesis and characterisation of ligands

The invention will now be exemplified by reference to the following experimental results relating to the synthesis of various ligands, their use in chelating various metal salts, and the subsequent stripping of both anions and cations from the ligands.

The ligands may be produced according to the following general reaction scheme, which is based on Schiff base type SALEN chemistry:



Where N* = a tertiary amine, for example a ring structure such as morpholine or piperidine.

The starting 2-hydroxy-5-alkyl benzaldehydes were prepared by the method of Levin (R. Aldred, R. Johnston, D. Levin, and J. Neilan, J. Chem. Soc. Perkin. Trans. 1, 1994, 1823) and the 4-ethoxymethyl morpholine/4-ethoxymethyl piperidines and hydroxy-3-(morpholin-4-yl-methyl)-benzaldehydes by the methods described by Fenton. (H. Adams, N. A. Bailey, D. E. Fenton, and G. Papageorgiou, J. Chem. Soc. Dalton. Trans., 1995, 1883).

Examples of these ligands were produced as follows:

Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] ethelene diamine (ligand 8).

2-Hydroxy-3-(morpholin-4-yl-methyl)-5-tert-butyl-benzaldehyde (6g, 21.7 mmol) was dissolved in diethyl ether (60ml) and added to a solution of ethane-1,2-diamine (0.636g, 10.6mmol) in ethanol (60ml). The resulting yellow solution was stirred overnight then concentrated in vacuo to give a yellow oil which on trituration in hexane at –78°C gave a waxy yellow solid. This was washed with hexane (15ml) and ether (15ml) and dried in vacuo (5.8 g, 95 %). m.p. 155-158 °C. (Found: C, 70.60; H, 9.06; N, 9.67. Calc. for $C_{34}H_{50}N_4O_4$: C, 70.56; H, 8.71; N, 9.68%). δ_H ($CDCl_3$, 200 MHz): 1.28 (s, 9H, $C(CH_3)_3$), 2.50 (t, $^3J_{HH}$ 4.6 Hz, 4H, NCH_2CH_2O), 3.58 (s, 2H, NCH_2CH_2N), 3.71 (t, $^3J_{HH}$ 4.6 Hz, 4H, NCH_2CH_2O), 3.90 (s, 2H, Ar-CH_2N), 7.14 (d, 1H, $^4J_{HH}$ 2.5 Hz, Ar-H), 7.37 (d, 1H, $^4J_{HH}$ 2.5 Hz, Ar-H), 8.37 (s, 1H, N=CH), 13.23 (s, br, 1H, OH). δ_C ($CDCl_3$): 31 (CH_3), 34 ($C(CH_3)_3$), 53 (NCH_2CH_2O), 57 (CCH_2N), 60 (NCH_2CH_2N), 67 (NCH_2CH_2O), 118 (Ar C), 124 (Ar C), 127 (Ar CH), 131 (Ar CH), 141 (Ar C), 157 (Ar C), 167 (CHN). MS (FAB, thioglycerol) m/z 579 (MH^+, 62 %).

Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] 1,3 – Diamino Propane (ligand 9).

5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde (6.000g, 21.7 mmol) was dissolved in diethyl ether (60ml) and poured into a solution of 1,3 – diamino propane (0.786g, 10.6mmol) in ethanol (60ml). Colour changed instantly to yellow and the solution was stirred overnight. Removing the solvent in vacuo gave the product as a dark yellow oil which was triturated in hexane at –78°C to produce a waxy yellow solid. Washed as above. MP 126-128 °C. Calculated for $C_{35}H_{52}N_4O_4$ – 70.91%C, 8.84%H, 9.45%N, found 70.15%C, 9.05%H, 9.37%N. FAB-MS m/z, normalised intensity, [assignment]: 594, 621.8% [MH^+]; 505, 18.9%, [M^+ - morph – 2H]; 422, base peak, [MH^+ - 2morph]. NMR ($CDCl_3$) ^1H: δ 1.30 (s, 9H, ^{t}Bu), 2.08 (t, J=6.5, 1H, centre propyl methylene), 2.52 (t, J=4.1, 4H, propyl and benzylic), 3.61, (s), and 3.66 (m, J=4.6, 8H, morpholinyl), 7.16 (d, J=2.5, 1H, aryl), 7.40 (d, J=2.5, 1H, aryl), 8.38 (s, 1H, imine), 13.51 (s,

broad, 1H, phenolic). ^{13}C δ: 30.80 (CH_3, ^tBu), 31.32 (CH_2, centre propyl methylene), 33.80 (q, ^tBu), 53.49 (CH_2, morpholinyl), 56.57, 56.65 (CH_2, benzylic/propyl), 66.90, (CH_2, morpholinyl), 117.68, 124.04 (q, aryl), 126.55, 130.88 (CH, aryl), 140.52, 157.32 (q, aryl) 165.53 (CH, aldehydic). FT-IR: (Dichloromethane film) 704cm^{-1} very strong, 737vs, 804w, 863s, 884m, 909m, 1007 and 1015 m doublet, 1032w, 1070m, 1116vs (dialkyl ether a.s. stretch), 1206m, 1265vs, 1303w, 1331w, 1363w, 1457w, 1457s, 1483s, 1633s, 2860vs and 2963vs (CH stretch), 3052m, 3940vw, 4195vw.

Characterisation of – N,N′ - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] trans – 1,2 – diamino cyclohexane (ligand 10).

Ligand 10 was produced in a manner similar to ligands 8 and 9 above. This yellow solid was recrystallised from petroleum ether (40-60), collected by filtration and air-dried (1.080g, 79%). m.p. 103-106 °C. Found: C, 69.19; H, 9.17; N, 8.46. Calc. for $C_{38}H_{56}N_4O_4$: C, 72.12; H, 8.92; N, 8.89%. δ_H ($CDCl_3$, 200 MHz): 1.23 (s, 9H, $C(CH_3)_3$), 1.66 (m, br, 4H, cHex CH_2), 1.86 (m, br, 4H, cHex CH_2), 2.48 (t, $^3J_{HH}$ 4.5 Hz, 4H, NCH_2CH_2O), 3.30 (m, 1H, cHex NCH), 3.70 (t, $^3J_{HH}$ 4.5 Hz 4H, NCH_2CH_2O), 3.54 (s, 2H, Ar-CH_2N), 7.06 (d, 1H, $^4J_{HH}$ 2.4 Hz, Ar-H), 7.33 (d, 1H, $^4J_{HH}$ 2.4 Hz, Ar-H), 8.27 (s, 1H, N=CH), 13.5 (s, br, 1H, OH). δ_C ($CDCl_3$): 24.07 (cHex CH_2), 31.23 (CH_3), 31.43 (cHex CH_2) 33.70 ($C(CH_3)_3$), 53.08 (CCH_2N), 53.57 (NCH_2CH_2O), 56.65 (cHex CH_2), 59.58 (cHex CH_2), 66.84 (NCH_2CH_2O), 117.6 (Ar C), 124.0 (Ar C), 127 (Ar CH), 131 (Ar CH), 141 (Ar C), 157 (Ar C), 165 (CHN). MS (FAB, thioglycerol) m/z 633 (MH^+, 42%).

Synthesis – Ethoxy–N–Morpholin-4–yl Methane.

Morpholine (87.12g, 1mole) was added dropwise to a suspension of paraformaldehyde (37.64g, 1.25 mol) and potassium carbonate (276.4g, 2mol) in ethanol (500ml) at 0°C with overhead mechanical stirring. When addition of morpholine was complete, the mixture was allowed to warm to room temperature and stirred vigorously for 48 hours. After this time, the solid

residues were filtered off and washed with ethanol (2 × 50ml), filtrate and washings were combined and concentrated under vacuum to leave a cloudy brown oil. This was distilled through a verigreux column under reduced pressure to give product as a clear, non-viscous liquid. BP 34°C at 0.3 mbar, Yield = 103.12g, 0.71 mol, 71%. Calculated for $C_7H_{15}O_2N$: 57.90%C, 10.41%H, 9.65%N, Found: 55.10%C, 10.37%H, 10.35%N, EI-MS: 100m/z, base peak, $[O(CH_2CH_2)_2NCH_2^+]$, no M^+ peak observed.

Synthesis –5-nonyl-Salicylaldehyde.

Magnesium methoxide catalyst was generated in situ by refluxing magnesium raspings (7.3g, 0.3 mol) and magnesium methoxide (1.75g of 7.4% w/w methanolic solution, 1.5 mmol) in methanol and toluene for 2 hours. When all the magnesium was dissolved and H_2 evolution had ceased 4-Nonyl phenol (112g, 0.5mol) was added and mixture was refluxed for a further hour. Toluene was added and the methanol –toluene azeotrope was removed by distillation at 85°C. A slurry of paraformaldehyde (45g, 1.5mol) in toluene was added to reaction over 50 minutes with concurrent removal of the volatile products by distillation. Stirring was continued at 95 – 100°C for 2 hours, then the mixture was cooled to room temperature. Solvent was removed under reduced pressure yielding the product as a pale yellow oil, purified by short path distillation under vacuum. B.P at 120°C at 1.0 mbar. NMR ($CDCl_3$) ^1H: δ 0.46 – 1.77 (m, J=1.2 – 6.4, 19H nonyl), 6.82 (d, J=9.2, 1H, aryl), 7.45 (m J=7-9, 2H, aryl), 9.88 (s, 1H, phenolic), 10.87 (s, 1H, aldehydic). ^{13}C δ:8.36 – 52.21 (nonyl), 116.94 (CH aryl), 119.90 (q, aryl), 130.42 (CH aryl), 135.42 (CH aryl) 159.22 (q, aryl), 196.81 (CH, aldehydic). FT-IR (NaCl plates, no nujol): 741w, 775w, 834w, 1167 and 1181 weak doublet, 1214 and 1231 w doublet, 1283s, 1378m, 1484s, 1589w, 1654vs (Carbonyl stretch), 2928s and 2960vs (CH stretch). EI-MS: 248, 10%, $[M^+]$. Calculated for $C_{16}H_{24}O_2$: 77.37%C, 9.74%H. Found: 77.54%C, 10.05%H.

Synthesis – 5-nonyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

Ethoxy-N-morpholin-4-yl methane (15.95g, 0.11mol) and 5-nonyl-Salicylaldehyde (24.8g, 0.1mol) were placed in a 500ml three-necked round bottomed flask and dissolved in acetonitrile (150ml). This solution was heated under reflux in an N_2 atmosphere for 66 hours, after which time solvent was removed under reduced pressure to yield product as a brown oil. Thin layer chromatography (1% methanol in chloroform) revealed that some unreacted aldehyde remained. The product was purified by flash chromatography. NMR ($CDCl_3$) ^1H δ: 0.42 – 1.70 (m, 194), 2.54 (s, 4H, morpholinyl), 3.68 (s) and 3.74 (t, J=4.6) 6H, morpholine and benzylic overlapping, 7.35 and 7.51 (m, J=2.4, 2H, aryl), 10.62 (m, J=2.3, 1H). Calculated for $C_{21}H_{33}NO_3$: 72.57%C, 9.57%H, 4.03%N. Found: 70.98%C, 9.48%H, 3.44%N. FT-IR: 610w,667w, 755vs, 801m, 835vw, 864vs, 909s, 969m, 1001m, 1019m, 1071m, 1118vs (dialkyl ether a.s. stretch), 1285s broad, 1381s, 1455vs broad, 1605s, 1651vs,1682vs, 2958vs broad (CH stretch). EI-MS: 347, 25.7% [M^+]. Synthesis – 5-tert-Butyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

Ethoxy-N-morpholinyl methane (15.95g, 0.11mol) and %-tert-Butyl Salicylaldehyde (14.8g 0.1mol) were dissolved in acetonitrile (150ml) and heated under reflux in an N_2 atmosphere for 24 hours. Thin layer chromatography (1% methanol in chloroform) revealed residual aldehyde but almost no morpholinyl methane in the reaction mixture, so extra morpholinyl methane (16.00g 0.11mol) was added and the mixture refluxed for a further 66 hours. TLC indicated that all the aldehyde had reacted, solvent was removed on a rotary evaporator yielding crude product as a pale green oil. Yield 39.427g, 140% suggesting that some acetonitrile remains in the oil. Mixture was dissolved in dichloromethane (150ml), washed with water (3 × 60ml) and concentrated in vacuo. NMR ($CDCl_3$) ^1H δ: 1.28 (s,9H, nonyl), 2.55 (m, J=4.6, 2H benzylic), 3.69 (m, J=2.1, 8.5H, morpholinyl), 7.03 (s) 7.37 (d, J=2.6) and 7.59 (d, J=2.6) (2H, aryl), 10.23 (s, 0.5H, aldehyde). ^{13}C δ:31.16 (CH_3, ^tBu), 33.96 (q, ^tBu), 52.99 (CH_2, morpholinyl), 59.34 (CH_2, benzylic), 66.65 (CH_2, morpholinyl), 81.53 (q, aryl), 88.34 (q, aryl), 125.63 (CH aryl), 133.41 (CH aryl)

133.41 and 158.60 (q, aryl), 192.59 (CH, aldehydic). FT-IR: 736w, 864m, 1118vs (dialkyl ether a.s. stretch), 1616m, 1269m, 1298vw, 1364vw, 1396vw, 1457s, 1481s, 1606m, 1653m, 1681s (carbonyl stretch), 2854s and 2960s (CH stretch). FAB-MS: (Matrix: THIO) 422, 3.6%, [M^+ + ^{t}Bu + morph + 2H].

Synthesis – 5-Methyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

5-Methylyl Salicylaldehyde (27.85g, 0,205 mol) and Ethoxy-N-morpholinyl methane (30.45g, 0.210mol) were refluxed together in acetonitrile (150ml) under an N_2 atmosphere for 48 hours. Reaction mixture was cooled to room temperature and concentrated in vacuo leaving a green oil. This was dissolved in HCl (2M, 100ml) and extracted in ether (3×80ml). The aqueous solution was then basified to pH 9 with 1M KOH, forming a yellow precipitate and a green oil. Yield 36.559g, 0.155mol, 75.8%. Calculated for $C_{13}H_{17}NO_3$: 66.36%C, 7.28%H, 5.95%N, Found: 65.86%C, 7.80%H, 6.82%N. EI-MS: 306, 1.3% [M^+ + 2CO + CH_3], FT-IR: 617m, 804m, 863vs, 909s, 953m, 994s, 1031m, 1071m, 1116vs (ether a.s. stretch), 1260vs, 1456 and 1472 vs doublet, 1498s, 1606vs, 1652vs (carbonyl stretch), 1682vs 2339 and 2359 w doublet, 2731w (aldehye CH stretch), 2852vs and 2960vs broad (CH stretch).

Synthesis – N,N′ - bis [5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde] ethelene diamine (ligand 12)

5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (2.824g, 8.13mmol) was dissolved in diethyl ether (30ml) and poured into a solution of ethylene diamine (0.243g, 4.05mmol) in ethanol (30ml). The colour instantly changed to yellow and after stirring overnight the resulting solution was concentrated in vacuo to give crude product as a yellow oil.

Synthesis – N,N′ - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane. (ligand 13) (ligand 13)

5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (3.30g, 9.50mmol) was dissolved in diethyl ether (30ml) and poured into a solution of diamino propane (0.348g, 4.70mmol) in ethanol (30ml), forming a yellow solution. Removing solvent in vacuo gave crude product as a yellow oil.

Synthesis – N,N′ - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] trans – 1,2 – diamino cyclohexane (ligand 14).

5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (2.92g, 8.40mmol) was dissolved in diethyl ether (30ml) and poured into a solution of trans – 1,2 – diamino cyclohexane (0.474g, 4.15mmol) in ethanol (30ml) to form a yellow solution. This was concentrated in vacuo to give the crude product as a yellow oil. $C_{48}H_{76}N_4O_4$

Characterisation of – N,N′ - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] ortho – Phenylene diamine (ligand 15).

The initial crude product was isolated as a viscous oil. Any remaining water-soluble impurities were extracted with water. The chloroform solution was evaporated to dryness and the product dried in-vacuo to yield a highly viscous yellow oil. (Found: C, 67.19; H, 8.25; N, 6.90. Calc. for $C_{48}H_{70}N_4O_4.(CHCl_3)$: C, 66.39; H, 8.07; N, 6.32%). δ_H ($CDCl_3$, 200 MHz): 0.5-1.69 (m, 19H, C_9H_{19} mixed isomer chain), 2.53 (s, 4H, NCH_2CH_2O), 3.72 (m, 6H, OCH_2CH_2N + Ar-CH_2N), 6.77 (m, 1H, Ar-H), 7.07 (m, 1H, Ar-H), 7.24-7.37 (m, 2H, Ar-H), 8.65 (s, 1H, CH=N), 13.50 (br, 1H, OH). δ_C ($CDCl_3$): 10-63 (C_9 mixed isomer chain), 52.8 (NCH_2CH_2O), 66.60 (NCH_2CH_2O), 66.70 (CCH_2N), 110.4 (Ar C), 114.6 (Ar C), 115.5 (Ar C), 118.1 (Ar C), 118.5 (Ar CH), 119.0 (Ar CH), 119.6 (Ar CH), 122.2 (Ar CH), 123.5 (Ar C), 127.2 (Ar CH), 127.7 (Ar CH), 153.6 (Ar C), 157.3 (CHN). MS (FAB, thioglycerol) m/z 768 (MH^+, 90%).

Synthesis – N,N′ - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] ortho – Phenylene diamine (ligand 11).

Ortho – phenylene diamine (2.163g, 20mmol) was dissolved in ethanol (150ml). The flask was wrapped in tin fiol to protect the material from light. This was added to a solution of 5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde (10.86g, 39.2mmol) in ether (150ml), again in the dark. After stirring for ca. 10 minutes the solution was concentrated in vacuo to leave a dark brown oil, crude yield = 11.36g, 18.4mmol, 93%. This was dissolved in hexane/ether 2:1 (ca 300ml). A small amount of brown solid remained undissolved and was removed by filtration. The solvent was allowed to evaporate slowly from a 500ml conical flask to leave a semi-crystalline orange material. This was dried under vacuum (oil pump) for 18 hours. Yield = 10.07g, 16.1mmol, 83.8%. FAB-MS 627, 8.5%, [MH$^+$], FT-IR (NaCl plates): 743m, 803w, 863m, 880w, 909w, 1005w, 1017vw, 1038w, 1070w, 1117vs (dialkyl ether a.s stretch), 1192vw, 1205vw, 1270vw, 1300w, 1362w, 1394w, 1456m, 1482m, 1494m, 1590m, 1616m (conjugated imine), 2856s and 2959vs (CH stretch), 3361s, broad, NMR ($CDCl_3$), ^1H δ: 1.18-1.34 (m, J=8 and J=12, 9H, ^tBu), 2.46 – 2.57 (m, J=4.6, 4H, morpholine), 3.62-3.76 (m, J=7.0, morph + benzylic 6H), 6.68 – 7.43 (3m's, J= 1.4, 1.2, 2.0, 4H, aryl), 8.67 (s, ½H, imine).

Synthesis of N,N'-bis [5-tert-Butyl-3-(piperidyl methyl) salicilaldeyde]-2,2'-diphenylene diamine (ligand 19).

To a stirred solution of 2-hydroxy-3-(piperidinyl-4-ylmethyl)-5-tert-butylbenzaldehyde (1.908 g, 6.93 mM) in ether (20 cm^3) was added a solution of 2,2'-diaminobiphenyl (0.638 g, 3.46 mM) in acetone (20 cm^3). The yellow solution was stirred overnight and concentrated in-vacuo to yield a pale yellow powder, which was recrystallised from acetone (1.407 g, 58%). Found: C, 78.96; H, 8.40; N, 7.90. Calc. for $C_{46}H_{58}N_4O_2$: C, 79.04; H, 8.36; N, 8.02%. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.24 (s, 9H, $C(CH_3)_3$), 1.42 (d, $^3J_{HH}$ 4.4 Hz, 2H, $NCH_2CH_2CH_2$), 1.58 (t, $^3J_{HH}$ 4.4 Hz, 4H, $NCH_2CH_2CH_2$), 2.41 (s, 4H, $NCH_2CH_2CH_2$), 3.51 (s, 2H, Ar-CH_2N), 7.10-7.44 (m, 6H, Ar-H), 8.50 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 24.19 ($NCH_2CH_2CH_2$), 25.88 ($NCH_2CH_2CH_2$), 31.28 (CH_3), 33.76 ($C(CH_3)_3$), 54.03 ($NCH_2CH_2CH_2$), 56.93 (CCH_2N), 118.08 (Ar C), 118.6 (Ar C), 124.3 (Ar C), 126.10 (Ar CH), 126.44 (Ar

CH), 128.63 (Ar CH), 130.72 (Ar CH), 131.04 (Ar CH), 134.5 (Ar C), 140.46 (Ar C), 147.9 (Ar C), 153.8 (Ar C), 162.08 (CHN). MS (FAB, NOBA) 699 m/z, (MH^+ 75%).

Characterisation of N,N' - bis [5 - nonyl - 3 - (piperidyl methyl) salicilaldehyde] 2,2'-diphenylene diamine (ligand 21)

This bright orange solid was isolated from the crude product after water-soluble impurities were removed by extraction with water (3.45 g, 95%). (Found: C, 80.16; H, 9.18; N, 6.71. Calc. for $C_{56}H_{78}N_4O_2$: C, 80.14; H, 9.37; N, 6.68 %). ^1H NMR ($CDCl_3$, 200 MHz): δ 0.48-1.37 (m, 19H, C_9H_{19} mixed isomer chain), 1.42 (s, 2H, $NCH_2CH_2CH_2$), 1.56 (s, 4H, $NCH_2CH_2CH_2$), 2.39 (s, 4H, $NCH_2CH_2CH_2$), 3.52 (s, 2H, Ar-CH_2N), 7.07-7.43 (m, 6H, Ar-H), 8.53 (s, 1H, CH=N), 12.5 (br, 1H, OH). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 24.81 ($NCH_2CH_2CH_2$), 26.53 ($NCH_2CH_2CH_2$), 31.28 (CH_3), 33.76 ($C(CH_3)_3$), 54.58 ($NCH_2CH_2CH_2$), 57.36 (CCH_2N), 116.2 (Ar CH), 118.8 (Ar CH), 119.1 (Ar CH), 125.0 (Ar C), 126.6 (Ar CH), 129.08 (Ar CH), 131.4 (Ar CH), 135.1 (Ar C), 137.8 (Ar C), 139.8 (Ar C), 148.2 (Ar C), 157.5 (Ar C), 162.8 (CHN). MS (FAB, thioglycerol) m/z, (MH^+ %).

Complexation

Complexation studies using ligands of the invention and various metal salts were carried out using the following general method. A solution of ligand (0.3 mM) in methanol (20 cm^3) was stirred together with a solution of the appropriate metal salt MX_n (1 M equiv.) in methanol (20 cm^3) overnight. Colour changes due to complex formation were generally instantaneous. After removal of the solvent in-vacuo the products were recrystallised as indicated and air-dried.

[Ni(8)SO_4], MX_n = $NiSO_4.6H_2O$. Recrystallisation from MeOH:H_2O, 3:1 gave a red microcrystalline material formulated as [Ni(1)SO_4]·$6H_2O$ (0.59 g, 93.6 %) m.p. 235-240 °C. (Found: C, 48.86; H, 7.37; N, 6.53. Calc. for $C_{34}H_{62}N_4NiO_7S$ C, 48.53; H, 7.43; N, 6.66%).χ_m = 1.14×10^{-9}, μ_{eff} = 0. δ_H ($CDCl_3$, 200 MHz)

1.27 (m, 9H, $C(CH_3)_3$), 2.6-3.3 (br, 4H, NCH_2CH_2O), 3.49 (s, 2H, NCH_2CH_2N), 3.7-4.2 (br, 4H, NCH_2CH_2O), 4.3 (s, 2H, Ar-CH_2N), 7.21 (d, 1H, $^4J_{HH}$ 2.5 Hz, Ar-H), 7.29 (d, 1H, $^4J_{HH}$ 2.5 Hz, Ar-H), 7.67 (s, 1H, N=CH). MS (FAB, thioglycerol) m/z 733 (MH^+, 10%). ν_{max}/cm^{-1} 1119vs (SO_4).

[Ni(8-2H)], MX_n = $Ni(CH_3CO_2)_2.4H_2O$. Recrystallisation from diethylether gave an orange/red microcrystalline material formulated as $[Ni(1\text{-}2H)]\cdot 2H_20$ (0.167 g, 73%) m.p. 235-240 °C. Found: C, 61.00; H, 7.38; N, 8.19. Calc. for $C_{34}H_{52}N_4NiO_4$: C, 60.77; H, 7.75; N, 8.34%. $\chi_m = 2.47 \times 10^{-10}$, $\mu_{eff} = 0$. δ_H ($CDCl_3$, 200 MHz): 1.24 (m, 9H, $C(CH_3)_3$), 2.53 (t, 4H, $^4J_{HH}$ 4.4 Hz, NCH_2CH_2O), 3.35 (s, 2H, NCH_2CH_2N), 3.61 (s, 2H, Ar-CH_2N), 3.73 (t, 4H, $^3J_{HH}$ 4.4 Hz, NCH_2CH_2O), , 6.89 (d, 1H, $^4J_{HH}$ 2.6 Hz, Ar-H), 7.37 (d, 1H, $^4J_{HH}$ 2.6 Hz, Ar-H), 7.46 (s, 1H, N=CH). MS (FAB, thioglycerol) m/z 636 (MH^+, 50%).

[Ni(8)$(NO_3)_2$], MX_n = $Ni(NO_3)_2.6H_2O$. Recrystallisation from diethylether gave an orange/red microcrystalline powder formulated as $[Ni(1)(NO_3)_2]\cdot 3H_2O$ (0.253 g, 91%) m.p. 200-204 °C. Found: C, 49.79; H, 6.35; N, 10.76. Calc. for $C_{34}H_{56}N_4NiO_{13}$: C, 50.11; H, 6.88; N, 10.31%. $\chi_m = 2.11 \times 10^{-10}$, $\mu_{eff} = 0$. δ_H ($CDCl_3$, 200 MHz): 1.24 (m, 9H, $C(CH_3)_3$), 3.21 (br, 4H, NCH_2CH_2O), 3.45 (s, 2H, NCH_2CH_2N), 3.91 (br, 4H, NCH_2CH_2O), 4.23 (s, 2H, Ar-CH_2N), 7.22 (d, 1H, $^4J_{HH}$ 2.1 Hz, Ar-H), 7.49 (d, 1H, $^4J_{HH}$ 2.1 Hz, Ar-H), 7.65 (s, 1H, N=CH). ν_{max}/cm^{-1} 1366vs and 1398vs (NO_3). MS (FAB, thioglycerol) m/z 699 (MH^+, 4%).

[Cu(8)SO_4], MX_n = $CuSO_4.5H_2O$. Recrystallisation from EtOH:ether, gave a dark brown crystalline material formulated as $[Cu(1)SO_4]\cdot 5H_2O$ (0.111 g, 43%). m.p. 268-270 °C. (Found: C, 51.96; H, 7.05; N, 6.33. Calc. for $C_{34}H_{60}N_4CuO_{13}S$: C, 52.44; H, 7.77; N, 6.80%). ν_{max}/cm^{-1} 1119vs (SO_4). MS (FAB, NOBA) m/z 734 (MH^+, 30%).

Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane (ligand 9) Nickel Sulphate complex.

Nickel Sulfate heptahydrate (104mg, 0.37mmol) was dissolved in hot methanol (20ml) and added to a hot solution of N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane (200mg,0.37mmol) in methanol (30ml). Mixture instantly turned brown. 20ml of solution was removed and concentrated in vacuo leaving a glassy brown solid, the remainder was left to stand in a sealed conical flask. The solid was crystallised in ether and recovered by filtration, yield = 95mg. Assuming sample is representative of whole solution, yield = 238mg, 0.32mmol, 86%.

Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane (ligand 9) Nickel Nitrate complex.

Nickel Nitrate hexahydrate (85mg, 0.37mmol) in methanol (20ml) was added to a hot solution of N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane (200mg,0.37mmol) in methanol (30ml), changing colour to brown. After stirring for ca. 5 minutes, 15ml solution was removed and concentrated invacuo and the rest was put aside to stand in a sealed conical flask. Removing the solution gave a brown amorphous solid which was crystalised in ether and recovered by filtration.

Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] Ortho- Phenylene diamine Nickel Sulfate complex.

A small amount of ligand (037g, 0.6mmol) was dissolved in methanol and stirred up with stoichiometric amount of nickel sulfate (1669mg, 0.6mol) forming a red brown solution. The solvent was removed in vacuo leaving a brittle red brown glass This was ground to a powder and found to be soluble in polar and chlorinated solvents, sparingly soluble in toluene and insoluble in hexane.

Solvent extraction and stripping

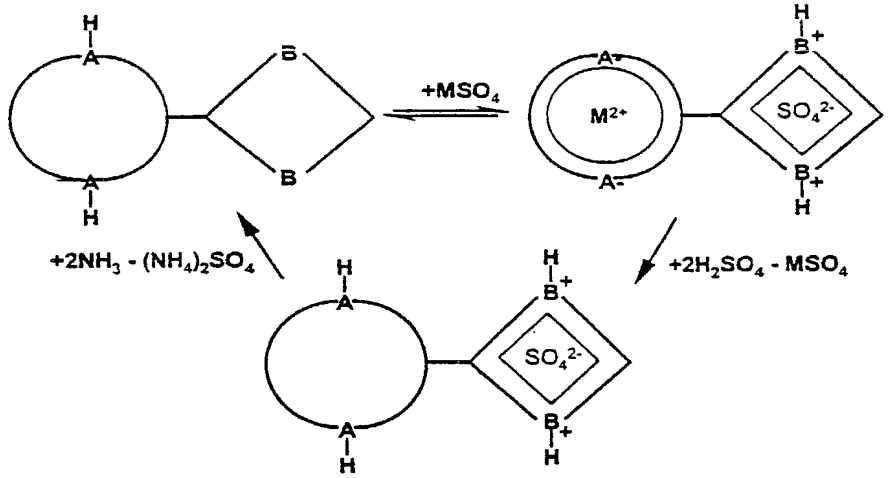
Solvent extraction and stripping of anions and cations is illustrated with

reference to the following example involving copper sulfate complexed with ligand 21.

A 0.01 M chloroform solution of ligand 21 (20 cm^3) was intimately mixed with a 1 M aqueous solution of $CuSO_4$ (20 cm^3) for 24 h at room temperature. The chloroform solution turned dark brown almost immediately. A sample was removed for ICP-EAS analysis to determine the copper and sulfur content. The remaining organic solution was washed with an aqueous solution (17 cm^3) adjusted to pH 1.5 with H_2SO_4 for 24 h. At this time the dark brown colour had bleached and the copper and sulfur content was again examined by ICP-EAS. The remaining organic solution was washed with an aqueous solution adjusted to pH 10 with ammonia for 24 h at which point the copper and sulfur content was examined by ICP-EAS. The chloroform solution was isolated and contacted with a 1 M aqueous solution of $CuSO_4$ (15 cm^3) for 24 h. The final copper and sulfur content of the organic phase was then determined. The percentage of copper and sulfate in the chloroform phase after each stage are displayed in the table below:

	Loading	Acid wash	Ammonia wash	Reloading
%Cu	83	22	23	73
$\%SO_4$	136	85	0	115

These results confirm that the ligand can be taken through a cycle of loading and stripping as represented in the scheme below. They also confirm the ability to fine-tune these ligands to suit a particular metal salt combination. In these experiments a biphenyl-bridged ligand 21 was used to encourage a tetrahedral metal binding environment so that copper binding is weakened favouring removal by acid stripping.


+MSO4
M2+
SO4 2-
+2NH3 - (NH4)2SO4
+2H2SO4 - MSO4

CLAIMS

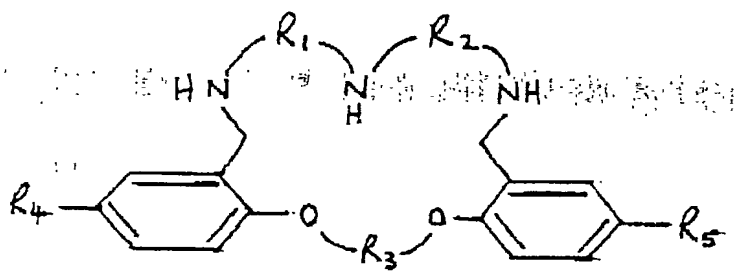
1. A method of extracting both the cation(s) and anion(s) of a metal salt from an aqueous medium, the method comprising the step of contacting the aqueous medium with a bifunctional ligand capable of binding both said cation(s) and said anion(s) so as to form a complex comprising said ligand and said cation(s) and anion(s).

2. A method according to claim 1, further comprising the steps of: selectively stripping and recovering said cations(s) and said anions(s) from said complex; and recovering said ligand, free of said cations(s) and anion(s), for future use.

3. A method according to claim 1 or claim 2, wherein the ligand has a greater affinity for a water-immiscible extraction medium than it does for said aqueous medium, the method involving the steps of: adding a said water-immiscible extraction medium to said aqueous medium, whereby said ligand with said cation(s) and said anion(s) bound thereto is partitioned preferentially in a water-immiscible phase; and separating said water-immiscible phase with said ligand-bound cation(s) and anion(s) therein from said aqueous medium.

4. A method according to claim 1 or claim 2, wherein the ligand is immobilised on or within a solid support.

5. A method according to any preceding claim, wherein the ligand is of the following formula:



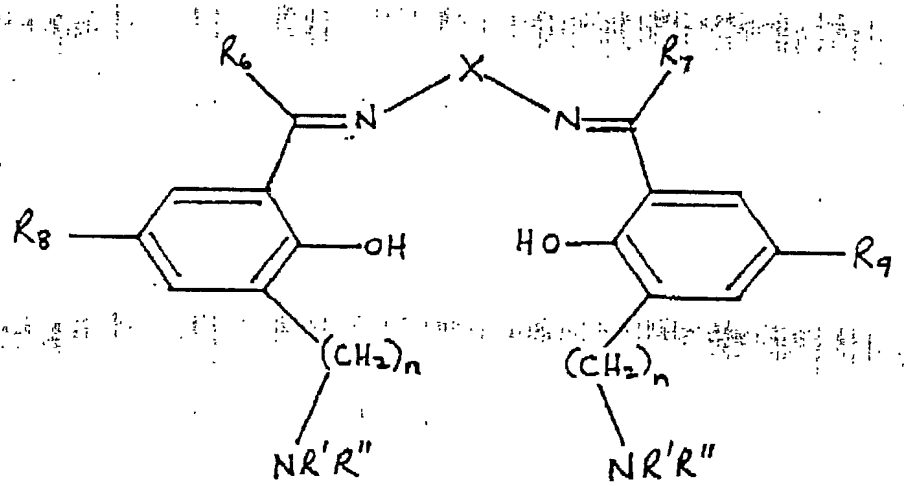
where R_1, R_2 and R_3 are, independently, substituted C_2 to C_4 linkages; and

R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

6. A method according to claim 5, comprising the further steps of: contacting the ligand-bound salt with an aqueous ammoniacal solution to produce an aqueous ammoniacal solution of the metal salt; and electrolysing said solution to produce elemental metal and an ammonium salt.

7. A method according to any of claims 1 to 4, wherein the ligand has a cation binding site comprising at least one coordinating acid group and an anion binding site comprising at least one protonatable base.

8. A method according to claim 5, wherein the ligand has the following formula:



where X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n = 2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

R'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring.

9. A method according to claim 7 or claim 8, comprising the further steps of: contacting the ligand-bound salt with a strong acid to protonate the ligand and release the metal cation(s); and electrolysing the resulting solution to product elemental metal.

10. A method according to claim 9, comprising the further step of contacting the ligand-bound anion(s) with an ammoniacal solution, to neutralise said solution and produce an ammonium salt.

11. A method according to any of claims 8 to 10, wherein NR'R" is a morpholine or piperidine ring.

ABSTRACT OF THE INVENTION

A method of removing both the cations and the anions of a metal salt from an aqueous medium, by use of a ligand having binding sites for the cations and anions. The cation binding site comprises at least one coordinating acid group and the anion binding site comprises at least one protonatable base. Using ligands of this type, both the anions and the cations may be selectively stripped from the ligand and recovered, and the ligand may thereby be recycled for future use.

Practitioner's Docket No. _____ ***PATENT***

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL, CONTINUATION, OR C-I-P)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type:

(check one applicable item below)

☐ original.

☐ design.

☐ supplemental.

NOTE: If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.

☒ national stage of PCT.

NOTE: If one of the following 3 items apply, then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR C-I-P.

NOTE: See 37 C.F.R. § 1.63(d) (continued prosecution application) for use of a prior nonprovisional application declaration in the continuation or divisional application being filed on behalf of the same or fewer of the inventors named in the prior application.

☐ divisional.

☐ continuation.

NOTE: Where an application discloses and claims subject matter not disclosed in the prior application, or a continuation or divisional application names an inventor not named in the prior application, a continuation-in-part application must be filed under 37 C.F.R. § 1.53(b) (application filing requirements — nonprovisional application).

☐ continuation-in-part (C-I-P).

INVENTORSHIP IDENTIFICATION

WARNING: If the inventors are each not the inventors of all the claims, an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor *(if only one name is listed below)* or an original, first and joint inventor *(if plural names are listed below)* of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONS

SPECIFICATION IDENTIFICATION

the specification of which:

(complete (a), (b), or (c))

(a) ☐ is attached hereto.

NOTE: *"The following combinations of information supplied in an oath or declaration filed on the application filing date with a specification are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.63:*

"(1) name of inventor(s), and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration on filing;

"(2) name of inventor(s), and attorney docket number which was on the specification as filed; or

"(3) name of inventor(s), and title which was on the specification as filed."

Notice of July 13, 1995 (1177 O.G. 60).

(b) ☐ was filed on _____, as ☐ Serial No. 0 /_____ or ☐ _____ and was amended on _____ *(if applicable).*

NOTE: *Amendments filed after the original papers are deposited with the PTO that contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 CFR 1.67.*

NOTE: *"The following combinations of information supplied in an oath or declaration filed after the filing date are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.63:*

"(1) name of inventor(s), and application number (consisting of the series code and the serial number; e.g., 08/123,456);

"(2) name of inventor(s), serial number and filing date;

"(3) name of inventor(s) and attorney docket number which was on the specification as filed;

"(4) name of inventor(s), title which was on the specification as filed and filing date;

"(5) name of inventor(s), title which was on the specification as filed and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration; or

"(6) name of inventor(s), title which was on the specification as filed and accompanied by a cover letter accurately identifying the application for which it was intended by either the application number (consisting of the series code and the serial number; e.g., 08/123,456), or serial number and filing date. Absent any statement(s) to the contrary, it will be presumed that the application filed in the PTO is the application which the inventor(s) executed by signing the oath or declaration."

Notice of July 13, 1995 (1177 O.G. 60), M.P.E.P. § 601.01(a), 6th ed., rev. 3.

(c) ☒ was described and claimed in PCT International Application No. PCT/GB00/01251, filed on March 31, 2000 and as amended under PCT Article 19 on _____ *(if any).*

SUPPLEMENTAL DECLARATION (37 C.F.R. § 1.67(b))

(complete the following where a supplemental declaration is being submitted)

☐ I hereby declare that the subject matter of the

☐ attached amendment

☐ amendment filed on _____

was part of my/our invention and was invented before the filing date of the original application, above-identified, for such invention.

ACKNOWLEDGEMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, § 1.56,

(also check the following items, if desired)

☐ and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent, and

☐ in compliance with this duty, there is attached an information disclosure statement, in accordance with 37 CFR 1.98.

PRIORITY CLAIM (35 U.S.C. §§ 119(a)–(d))

NOTE: "The claim to priority need be in no special form and may be made by the attorney or agent if the foreign application is referred to in the oath or declaration as required by § 1.63. The claim for priority and the certified copy of the foreign application specified in 35 U.S.C. 119(b) must be filed in the case of an interference (§ 1.630), when necessary to overcome the date of a reference relied upon by the examiner, when specifically required by the examiner, and in all other situations, before the patent is granted. If the claim for priority or the certified copy of the foreign application is filed after the date the issue fee is paid, it must be accompanied by a petition requesting entry and by the fee set forth in § 1.17(i). If the certified copy is not in the English language, a translation need not be filed except in the case of interference; or when necessary to overcome the date of a reference relied upon by the examiner; or when specifically required by the examiner, in which event an English language translation must be filed together with a statement that the translation of the certified copy is accurate." 37 C.F.R. § 1.55(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §§ 119(a)–(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

(d) ☐ no such applications have been filed.

(e) ☒ such applications have been filed as follows.

NOTE: Where item (c) is entered above and the International Application which designated the U.S. itself claimed priority check item (e), enter the details below and make the priority claim.

PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119(a)–(d)

COUNTRY (OR INDICATE IF PCT)	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 37 USC 119
GB	9907485.8	31 March 1999	☒ YES NO ☐
			☐ YES NO ☐
			☐ YES NO ☐
			☐ YES NO ☐
			☐ YES NO ☐

CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)

(34 U.S.C. § 119(e))

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

PROVISIONAL APPLICATION NUMBER — FILING DATE

_____ /_____ _____

_____ /_____ _____

_____ /_____ _____

CLAIM FOR BENEFIT OF EARLIER US/PCT APPLICATION(S) UNDER 35 U.S.C. 120

☐ The claim for the benefit of any such applications are set forth in the attached ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CONTINUATION-IN PART (C-I-P) APPLICATION.

ALL FOREIGN APPLICATION(S), *IF ANY*, FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

NOTE: *If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR C-I-P APPLICATION for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. § 120.*

POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

(list name and registration number)

Stanley B. KITA, Registration No. 24,561; George A. SMITH, Jr., Registration No. 24,442; Mary E. BAK, Registration No. 31,215; William BAK, Registration No. 37,277; Henry HANSEN Registration No. 19,612 and Cathy Ann KODROFF, Registration No. 33,980

6

(check the following item, if applicable)

☐ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

☒ Attached, as part of this declaration and power of attorney, is the authorization of the above-named practitioner(s) to accept and follow instructions from my representative(s).

NOTE: *"Special care should be taken in continuation or divisional applications to ensure that any change of correspondence address in a prior application is reflected in the continuation or divisional application. For example, where a copy of the oath or declaration from the prior application is submitted for a continuation or divisional application filed under 37 CFR 1.53(b) and the copy of the oath or declaration from the prior application designates an old correspondence address, the Office may not recognize, in the continuation or divisional application, the change of correspondence address made during the prosecution of the prior application. Applicant is required to identify the change of correspondence address in the continuation or divisional application to ensure that communications from the Office are mailed to the current correspondence address. 37 CFR 1.63(d)(4)." § 601.03, M.P.E.P., 7th Edition.*

SEND CORRESPONDENCE TO	**DIRECT TELEPHONE CALLS TO:** *(Name and telephone number)*
☒ Address HOWSON AND HOWSON Spring House Corporate Center, P.O. Box 457 Spring House, Pennsylvania 19477 ☒ Customer Number 00270	(215) 540-9200

(complete the following if applicable)

Since this filing is a ☐ continuation ☐ divisional there is attached hereto a Change of Correspondence Address so that there will be no question as to where the PTO should direct all correspondence.

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

NOTE: Carefully indicate the family (or last) name, as it should appear on the filing receipt and all other documents.

Full name of sole or first inventor

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Full name of second joint inventor, if any

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Full name of third joint inventor, if any

(GIVEN NAME) | (MIDDLE INITIAL OR NAME) | (FAMILY OR LAST NAME)

Inventor's signature _____

Date _____ **Country of Citizenship** _____

Residence _____

Post Office Address _____

(check proper box(es) for any of the following added page(s) that form a part of this declaration)

☐ **Signature** for fourth and subsequent joint inventors. *Number of pages added* _____.

* * *

☐ **Signature** by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. *Number of pages added* _____.

* * *

☐ **Signature** for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR 1.47. *Number of pages added* _____

* * *

☐ Added page for **signature** by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 CFR 1.47)

* * *

☐ Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application.

☐ Number of pages added _____

* * *

☒ Authorization of practitioner(s) to accept and follow instructions from representative.

* * *

(if no further pages form a part of this Declaration, then end this Declaration with this page and check the following item)

☐ This declaration ends with this page.

ADDED PAGE TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR AUTHORIZATION OF ATTORNEY(S) TO ACCEPT AND FOLLOW INSTRUCTIONS FROM REPRESENTATIVE

The undersigned to this declaration and power of attorney hereby authorizes the U.S. attorney(s) named herein to accept and follow instructions from

JY & GW Johnson

Name(s) of authorized representative(s)

Kingsbourne House,

Address

229-231 High Holborn,

London WC1V 7DP ENGLAND

as to any actions to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorney(s) and the undersigned. In the event of a change in the person(s) from whom instructions may be taken, the U.S. attorney(s) will be so notified by the undersigned.